Preparation of water-soluble and water-swellable starch acetates using microwave heating[☆]

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Abstract

Starch acetates of degree of substitution 0.1–1.5 were prepared by heating corn starch, acetic acid and acetic anhydride in sealed, stirred, teflon vessels in a microwave reactor. Reaction efficiencies were typically >90% at reaction temperatures of 150–160 °C for 4–7 min. Starch acetates prepared by reaction at 160 °C to DS values of 0.4–0.9 were >90% soluble in room temperature water. Acetylation rates and water solubilities decreased in the order waxy > normal > high amylose starch. Significant reduction in molecular weights of the starches occurred during microwave reactions. Acetylation occurred preferentially at the C6 position (70%) based on 13C NMR results. Acetylation at lower temperatures (120 °C) gave starches of DS 0.2–0.3 which were water insoluble but highly swellable. These starches retained their native crystallinity, implying that acetate substitution was a block pattern. Published by Elsevier Ltd.

Keywords: Starch ester; Microwave; Esterification; Biodegradable

1. Introduction

Non-degradable, petroleum-based, water soluble polymers such as polyacrylates, polyacrylamides and polyvinyl acetates are used extensively in applications such as thickeners, paper coatings, textile sizes, dispersants, water treatment and detergents (Meltzer, 1976). They are often disposed of through wastewater and thus find their way into rivers, lakes and drinking water. Biopolymers are, however, being considered for these uses, as they are biodegradable and based on renewable resources such as corn (Swift, 2002). Modified starches may be attractive candidates as they are inexpensive and can have a wide functionality.

Modified starches such as starch acetates are prepared commercially by reaction of an aqueous suspension of starch granules with acetic anhydride and sodium hydroxide (Rutenberg & Solarek, 1984; Jarowenko, 1986). Such aqueous suspension reactions are favored, since byproducts of reaction can be easily removed by filtration and washing with water. These reactions are, however, rather inefficient (~70%) due to

side reaction of anhydride with water as well as the large amounts of sodium hydroxide needed to maintain pH 8–9 during reaction (Rutenberg & Solarek, 1984; Tessler & Billmers, 1996). In addition, the products usually have low water solubility, even after heating, and there is a tendency to recrystallize (retrograde) over time. For granular starch reaction, substitution tends to take place near the amorphous, branched regions leaving unsubstituted side chains to self-associate (Hood & Mercier, 1978; Richardson & Gorton, 2003).

Starch acetates of moderate to high DS have been prepared under homogeneous conditions using solvents such as DMSO, DMAc/LiCl, DMF and pyridine (Rutenberg & Solarek, 1984). Such solvents are, however, rather expensive and toxic; hence their commercial use is not favorable.

The use of acetic acid as a solvent for acetylation of starch has been reviewed (Whistler, 1945; Degering, 1950; Rutenberg & Solarek, 1984). Although starch has been heated with acetic acid and acetic anhydride at reflux to produce starch acetates, long times (4–40 h) were required for reaction (Burkhard & Degering, 1942). Although starch acetates of <25% acetyl were claimed to have some water solubility, this was not quantified (Clarke & Gillespie, 1932). Starch acetates of DS 0.5–2.5 were prepared in acetic acid/anhydride using 50% aqueous NaOH as catalyst (Shogren, 1996; Xu, Miladinov & Hanna, 2004), but reaction efficiencies were <70% and much sodium acetate byproduct was produced. Some recent patents have described preparation of starch acetates by reactive extrusion but there is little information on the effects of formulation and processing conditions on structure and

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properties of the resulting acetates (Runkel, Stoye, Rpthel, & Kakusche, 1999; Lammers, Tiitola, & Vuorenpaa, 1998). Koroskenyi & McCarthy (2002) found that microwave heating accelerated the esterification and etherification of starches.

Recently, it was shown that starch acetates and other esters can be made very efficiently on a micro scale without added catalyst or water simply by heating dry starch with acetic acid and anhydride at 180 °C for 2–10 min (Shogren, 2003). At this temperature, starch will melt in acetic acid (Shogren, 2000), and thus, a homogeneous acetylation would be expected to occur. In order to scale up this process, microwave heating was chosen since it gives fast, uniform heating and sometimes enhanced reaction rates. The goal of the present work was to characterize the effects of microwave reaction conditions and starch type on the structure and physical properties of starch acetates. Properties of interest include water solubility, swellability, and viscosity.

2. Materials and methods

2.1. Materials

Normal corn starch (pure food grade) and waxy maize starch (7350) were purchased from A.E. Staley (Decatur, IL). High (70%) amylose corn starch (Hylon 7) and potato amylose were purchased from National Starch (Bridgewater, NJ). Starches were vacuum dried overnight at 110 °C before using. Glacial acetic acid and acetic anhydride (99 + %) were purchased from Aldrich (Milwaukee, WI).

2.1.1. Preparation of starch acetates

Typically, 70 g dry starch, 70 g acetic acid and 0–70 g acetic anhydride were added to a 270 ml teflon vessel. A magnetic stir bar was added and the mixture was stirred for 5 min. The vessel was then sealed, the thermocouple inserted and the vessel was heated in a microwave labstation 1600 (Milestone, Inc., Shelton, CT). Unless otherwise stated, the temperature ramp was 25–150 °C over 3.5 min, 150–160 °C over 1.5–4.5 min. Power to the microwave magnetron was automatically adjusted to give the linear temperature ramps entered into the computer control system. Maximum microwave power was limited to 650 W to avoid overshooting the temperature program. After opening the reactor, the contents were placed in a waring blendor with 500 ml ethanol and blended until the precipitate was broken into fine particles ($\sim$ 1 min). The ethanol supernatant was poured off and four additional ethanol extractions were performed. Excess ethanol was removed by filtration on a Buchner funnel and the starch acetates were dried in a forced air oven overnight at 50 °C and then in a vacuum oven overnight at 80 °C.

2.2. Analytical methods

Degree of substitution (DS) values were estimated using ^{1}H NMR as described previously (Shogren, 2003). Briefly, samples (2%) were dissolved and hydrolysed in 0.5 M NaOD and areas of acetyl CH_3 and starch CH resonances were measured. Reaction efficiencies were based on the amount of acetic anhydride added and were calculated as $RE = DS/(w_{aa}/$

$102)/(w_{cs}/162)$, where w_{aa} and w_{cs} are the weights of acetic anhydride and starch, respectively. ^{13}C DEPT-135 NMR spectra were obtained at 25 °C on a Bruker Ultrashield 500 at 125.76 MHz. Samples were dissolved in D_2O at 15% concentration by weight. Water solubilities were determined by stirring 0.5 g sample in 30 ml. water at room temperature for 20 min, centrifuging at 3000 rpm for 10 min, drying and weighing the supernatant. Water absorption was calculated as the weight of the centrifuged pellet divided by dry weight of the sample. Water solubility values were corrected for the fraction of soluble material present in the gel pellet using the following approximate equation:

$$WSI = 100 \frac{W_s V_t/(V_t - V_g)}{W_{sam}} \tag{1}$$

where W_{sam} = dry weight of sample (g), W_s = dry weight of supernatant (g), V_t = total volume of suspension centrifuged (ml) and V_g = volume of gel fraction (ml).

Intrinsic viscosities were determined as described previously for samples in 1 M KOH after hydrolysis for 1 day at 3 °C (Mark & Mehltretter, 1970). A Cannon–Ubbelohde #75 4-bulb viscometer in a 25 °C water bath was used.

3. Results and discussion

A typical microwave reactor heating profile is shown in Fig. 1. The actual temperature as measured by the thermocouple in the reactor oscillates around the temperature program set by the computer. Power to the magnetron is supplied in bursts as shown. After reaction and while still hot, the consistency of the reaction mixture was typically highly viscous or gel-like.

The effect of temperature on extent of acetylation and solubility/swelling properties for dry starch/glacial acetic acid/acetic anhydride (CS/GAA/AA 1/1/0.5) is shown in Table 1. This ratio of reactants was chosen, since preliminary work indicated that high water solubility was obtained under these conditions (see also Fig. 6). At low reaction temperatures (120 °C), acetylation was slow with DS values up to 0.3 obtained after 40 min. Water solubility was low for these samples but water absorption (WAI) was quite high (14 g/g). Although this level of
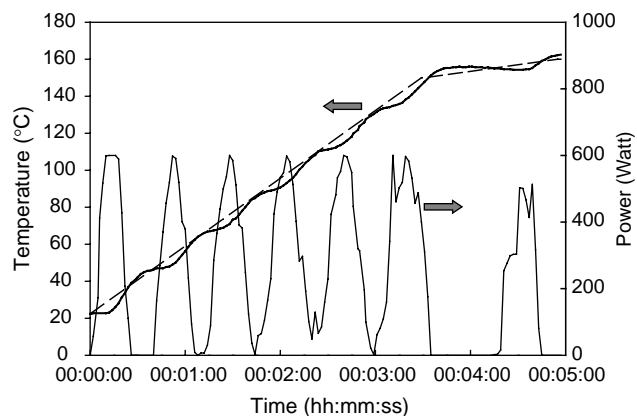

Fig. 1. Plots of temperature program (solid line), temperature inside microwave vessel (dashed line) and magnetron power for dry waxy maize starch/GAA/AA 70/70/35 w/w/w.

Table 1
Effect of temperature on composition and properties of starch acetates made from dry corn starch/glacial acetic acid/acetic anhydride 1/1/0.5 (w/w/w)

Temperature program[a]		DS[b]	RE (%)[c]	WSI (%)[d]	WAI (g/g)[e]
Ramp 1 (T, t)	Ramp 2 (T, t)				
25–120, 3.5	120, 10	0.19	24	12	10.6
25–120, 3.5	120, 20	0.21	26	15	13.1
25–120, 3.5	120, 40	0.30	38	2	13.6
25–150, 3.5		0.33	42	49	14.4
25–150, 3.5	150–160, 1.5	0.57	72	76	11.0
25–150, 3.5	150–160, 2.5	0.76 ± 0.02[f]	96 ± 3	91 ± 4	2.4 ± 0.9
25–150, 3.5	150–160, 5.0	0.74	93	93	1.4
25–175, 3.5		0.77	97	99	0.2

[a] T = temperature (°C); t = time (min).
[b] Degree of substitution.
[c] Reaction efficiency (based on acetic anhydride, see Section 2.2).
[d] Water solubility index.
[e] Water absorption index.
[f] Error estimates shown represent the mean and standard deviation from three repetitions of the experiment.

absorbency is less than that of superabsorbents, such a water absorbent starch polymer could have applications in medical, pharmaceutical or other areas. For reactions reaching 160 °C, acetylations were rapid, with DS values of 0.76 and reaction efficiencies of 96% after 6 min. Cold water solubilities of these starch acetates were over 90%. Acetylations were more rapid at reaction temperatures reaching 175 °C, with full acetylation occurring after 3.5 min. Colors of the starch acetates prepared by this method were white to light tan. Heating for longer times at 160–175 °C gave products which became more brown in color.

X-ray powder diffraction patterns for some starch acetates are shown in Fig. 2. Starch acetates made at low reaction temperature (120 °C) had the native A-type crystalline structure while those made at higher temperatures (160 °C) were mostly amorphous with a small amount of V-structure. At low temperatures, acetylation probably occurs in the amorphous regions of the starch granule, leading to swelling in those regions. Dissolution in water is not possible, however, due to strong associations through the crystalline outer branches of starch molecules so a gel results. At higher reaction temperatures, the native crystalline order is lost. Under these more homogeneous conditions, acetylation would be expected to be more uniform and result in greater water solubility. The small amount of V-structure probably results from amylose–acetic or amylose–fatty acid complexes which form on cooling for amylose molecules having unsubstituted regions (Shogren, 2000).

^{13}C DEPT and conventional ^{13}C NMR spectra for a starch acetate of DS 0.77 in D$_2$O are shown in Fig. 3(A) and (B). Based
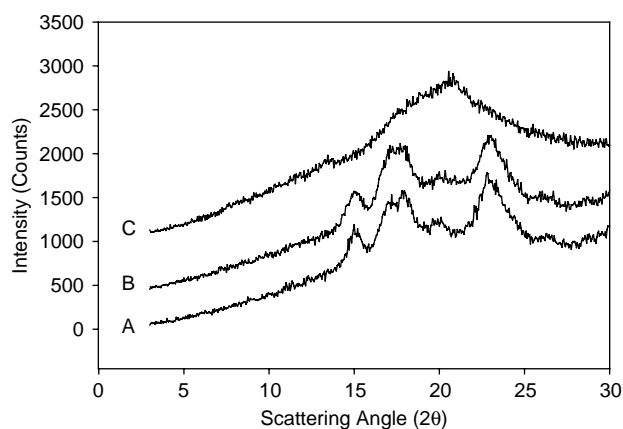
Fig. 2. X-ray powder diffraction scans for native corn starch (A), dry CS/GAA/AA 70/70/35 heated at 120 °C for 40 min (B) and dry CS/GAA/AA 70/70/35 heated to 160 °C over 6 min (C).
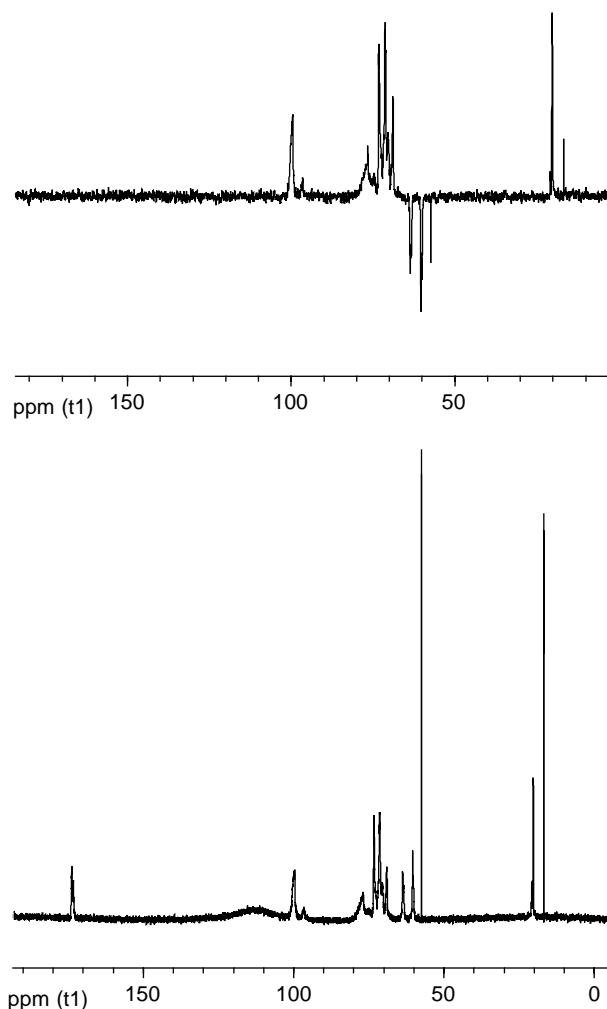
Fig. 3. DEPT (A) and regular (B) 13C NMR spectra of starch acetate, DS 0.77 in D$_2$0.
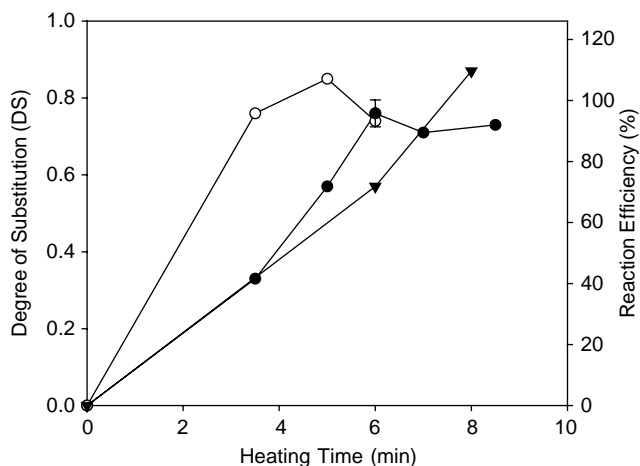
Fig. 4. Effect of microwave heating time on the degree of substitution and reaction efficiency of dry waxy (○), normal (●) and high amylose (▼) starches for mixtures of starch/GAA/AA 1/1/0.5 w/w/w. Reaction efficiencies based on acetic anhydride (see Section 2.2).
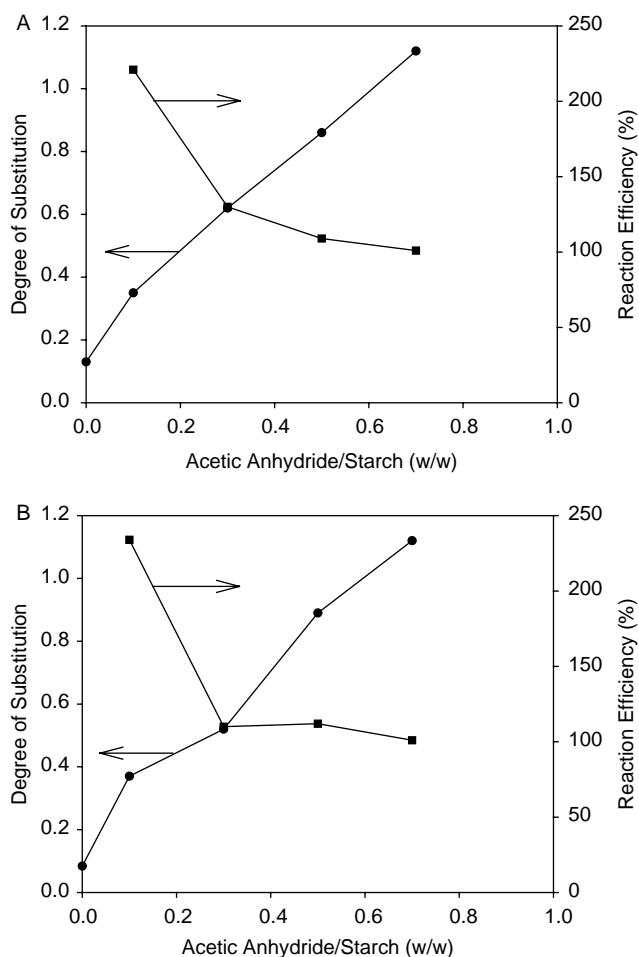

Fig. 5. Effect of acetic anhydride content on the degree of substitution (●) and reaction efficiency (■) of waxy maize (A) and high amylose starches (B). Heating programs were 25–150 °C over 3.5 min, 150–160 over 1.5 min. (A) and 25–150 °C over 3.5 min, 150–160 over 4.5 min (B). Reaction efficiencies based on acetic anhydride (see Section 2.2).

on assignments from Falk et al. (1997), the negative peaks in the DEPT spectrum can be assigned to C6 (60.3 ppm) and acetylated C6 (63.6 ppm). In the ^{13}C spectrum, the resonance at 99.9 ppm is assigned to C1 while the small resonance at 96.6 ppm is assigned to C1 with an adjacent acetylated C2. Similarly, the resonance at 76.9 ppm is assigned to C4 while the small resonance at 75.0 ppm is assigned to C4 with an adjacent acetylated C3. Based on the areas of these peaks, the percent acetylation at C2, C3 and C6 was approximately 15, 16, and 69%. The greater rate of reaction at the primary hydroxyl at C6 is likely due to lesser steric hindrance than at secondary hydroxyls of C2 and C3. This is consistent with previous work showing preference for reaction at C6 during homogeneous acetylation of cellulose in DMAc/LiCl and homogeneous reaction of amylose with diketene in DMSO (Yalpani, 1988).

The effect of starch type on the acetylation rate for reaction mixtures of starch/GAA/AA 1/1/0.5 is shown in Fig. 4. A DS value of 0.79 represents 100% reaction efficiency for this composition. For these experiments, reaction temperatures were increased linearly from 25 to 150 °C over 3.5 min then increased linearly from 150–160 °C over the remainder of the time indicated. Acetylation was most rapid for waxy starch, normal corn starch was intermediate and high amylose corn starch was slowest for reaction times >4 min. Reaction efficiencies reached close to 100% for waxy, normal and high amylose starches after 3.5, 6 and 8 min, respectively. The decreasing rate of reaction with increasing amylose content may be due to the presence of crystalline amylose or amylose complexes. These crystalline forms normally melt at a higher temperature than the native crystalline amylopectin component (Shogren, 1992) and thus would be more resistant to swelling and reaction.

The effect of amount of acetic anhydride on the extent of acetylation of waxy and high amylose starches is shown in Fig. 5.
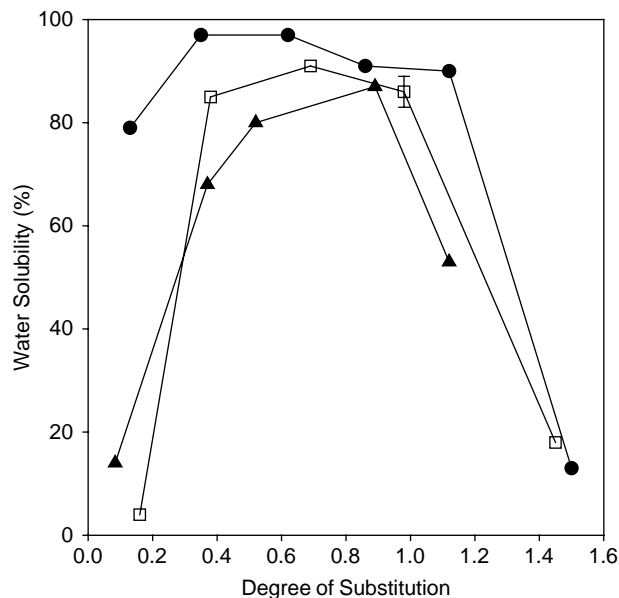

Fig. 6. Effect of degree of substitution on the water solubility of waxy (●), normal (□) and high amylose (▲) starch acetates. Heating programs were 25–150 °C over 3.5 min, 150–160 over 1.5 min (waxy), 25–150 °C over 3.5 min, 150–160 over 2.5 min (normal) and 25–150 °C over 3.5 min, 150–160 over 4.5 min (high amylose).
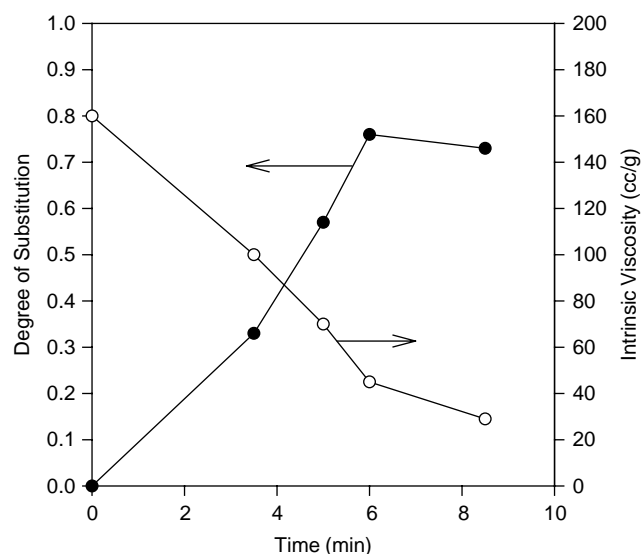
Fig. 7. Effect of microwave heating time on the degree of substitution (●) and intrinsic viscosity (○) of normal corn starch acetates. Composition was dry starch/GAA/AA 1/1/0.5 w/w/w and temperature program was 25–150 °C over 3.5 min, 150–160 for remainder of time.

For these experiments, total reaction times were 4.5 and 8 min for waxy and high amylose starch, respectively. Values for DS increased linearly with amount of acetic anhydride while reaction efficiency (based on weight of anhydride added) declined from > 200% at low anhydride to near 100% with more anhydride addition. The high apparent reaction efficiency at low anhydride addition reflects some direct acetylation of starch by acetic acid. Indeed, when dry starch and glacial acetic acid were reacted alone, a DS of approximately 0.1 was obtained.

The effect of DS on the water solubility of waxy, normal and high amylose starch acetates is shown in Fig. 6. Waxy starch acetates became fully cold water soluble at rather low DS (~0.3) while more acetylation was required to prepare water-soluble normal and high amylose starch acetates. This behavior is probably related to the presence of residual native crystallinity and/or the formation of crystalline amylose domains on heating that are slower to acetylate (see above). Such low DS domains consisting of presumably crystalline or retrograded amylose would be insoluble in water at room temperature. Water solubility begins to decrease at DS values over 1, probably due to increasing hydrophobicity from the acetyl groups. Intrinsic viscosities of starch acetates of DS between

0.17 and 1.0 were similar (50–68 ml/g) so changes in molecular weight with DS were rather small.

The effect of microwave heating time on the intrinsic viscosity of starch acetate (CS/GAA/AA 1/1/0.5) is shown in Fig. 7. Intrinsic viscosity decreases rapidly with heating time, reaching a value of 44 ml/g after 6 min compared with a value of 160 ml/g for unmodified corn starch. Previous studies of the viscosity of aqueous solutions of starch have also shown that high temperatures, particularly at pH < 3, result in reduction of starch molecular weight (Dintzis & Bagley, 1995; Dintzis & Fanta, 1996). Water produced by direct acetylation of starch with acetic acid can hydrolyse glycosidic linkages of starch causing reduction in viscosity and molecular weight. Acetolysis of glycosidic linkages of starch in acetic anhydride/acetic acid mixtures has also been shown to occur (Sutra, 1932; BeMiller, 1965).

The effect of starch type on the intrinsic viscosity of starch acetates is shown in Table 2. Intrinsic viscosity seems to increase with increasing amylose content of the corn starches. The reason for this behavior is not clear but larger decreases in viscosity for waxy starches than for normal or high amylose starches after exposure to high temperatures have been observed previously (Dintzis & Bagley, 1995). Using the Mark–Houwink relation for acid hydrolysed waxy maize starch in DMSO, $[n] = 1.84 \times 10^{-1} M_w^{0.36}$ for $[n] < 32$ and $[n] = 2.16 \times 10^{-3} M_w^{0.67}$ for $[n] > 32$ (Salemis & Rinaudo, 1984), one can estimate M_w values of 0.84×10^6, 2.9×10^6 and 4.2×10^6 for waxy, normal and high amylose starch acetates. These values are much lower than M_w for native starches, which range from $20–800 \times 10^6$, depending on solution conditions and starch type (Millard, Dintzis, Willett, & Klavons, 1997; Han & Lim, 2004; Aberle, Burchard, Vorwerg, & Radosta, 1994). Previous work has shown that the Mark–Houwink parameters for amylose in DMSO and 1 M KOH are quite similar (Cowie, 1961).

The effect of water content of starch on the reaction of starch, acetic acid and acetic anhydride was investigated briefly. For the microwave reaction of corn starch (10.5% water) at a ratio of CS/GAA/AA 1/1/0.5, heated from 25–150 °C for 3.5 min and 150–160 °C for 2.5 min, the DS obtained was 0.21. The latter is much lower than a DS of 0.77 obtained using dry starch, due to side reaction of water with acetic anhydride. A reaction of corn starch (10.5% water) and acetic anhydride at a ratio of CS/AA 1/1.04 was also carried out using a heating program of 25–140 °C for 3.5 min. After 3 min of heating, the internal temperature increased rapidly above the

Table 2

Effect of amylose content on composition and properties of starch acetates made from dry starch/glacial acetic acid/acetic anhydride 1/1/0.5 (w/w/w)

Base starch	Amylose (%)	DS[a]	RE[b]	WSI (%)[c]	I.V. (ml/g)[d]
Waxy maize	1	0.70	88	99	25 (178)
Normal corn	27	0.78	98	95	46 (160)
High amylose corn	70	0.57	72	70	59 (118)
Potato amylose	100	0.73	92	35	44 (120)

Temperature program was 25–150 (3.5 min), 150–160 (2.5 min).

[a] Degree of substitution.
[b] Reaction efficiency (based on acetic anhydride, see Section 2.2).
[c] Water solubility index.
[d] Intrinsic viscosity.

program and the contents of the vessel were expelled through the safety pressure release valve, giving a dry, white foamed material. This probably occurred due to the rapid acceleration of the exothermic reaction between the anhydride and water and starch. The resulting starch acetate had a DS of 0.98 and a water solubility of 87%. These reactions with ambient moisture corn starch were not pursued further due to their instability in the batch microwave reactor. However, such reactions may be more feasible in a flow-through microwave or extrusion system, where reaction temperatures may be more precisely controlled over short periods of time.

An interesting question arises as to whether there is a difference in acetylation rate between microwave and conventional conductive heating. A mixture of dry starch, acetic acid, and acetic anhydride (CS/GAA/AA 1/1/0.5) was heated in both the microwave reactor and in a sealed glass reacti-vial in a conventional block heater. By adjusting the block temperature to 200 °C, a temperature profile was obtained that was very similar to the microwave program. At the end of the 6 min total heating time, it was found that starch acetates prepared by microwave and conventional heating had DS 0.72 and 0.56, respectively. This suggests that there may be a small enhancement in the rate of acetylation using microwave radiation.

In summary, starch acetates of high cold water solubility with DS values of 0.3–1.1 were prepared quickly and efficiently by microwave heating of starch, acetic acid and acetic anhydride. The acetic acid can be removed by volatilization after reaction and reused, leaving no byproducts or wastewater. Molecular weights of the starch acetates were much lower than the native starches and hence, these modified starches may be of use for applications such as adhesives and paper and textile coatings where starches are normally treated with acid or amylases to reduce viscosities. Some of the starch acetate solutions exhibit foaming, suggesting surface activity. It was also observed that a starch acetate solution spread on a polyester film (Bionolle) while an unmodified starch solution beaded up. Surface properties of aqueous solutions of these starch esters are currently being studied in more detail. Starch acetates of DS 0.3 prepared at low temperatures had a high degree of swelling but also an intact crystalline structure. Such a modified starch might have value as an absorbent. Certainly, much more work is needed on the effects of substituent distribution on the properties of starch acetates and other modified starches.

Acknowledgements

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